PROCESS FOR EFFECTING ULTRA-DEEP HDS OF HYDROCARBON FEEDSTOCKS

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority from US Provisional Application 60/237892, filed October 4, 2000.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for effecting ultra-deep HDS of hydrocarbon feedstocks.

2. Prior Art

In an effort to regulate SO_2 emissions from the burning of fuels and to optimise the performance of tail-end catalysts, in particular exhaust treatment catalysts, the regulations as to the sulfur content of fuels, in particular diesel fuels, are becoming more and more strict. In Europe as of 2000 diesel feedstocks are required to have a sulfur content less than 350 ppm, while as of 2005, the sulfur content should be less than 50 ppm, with even further decreases not being excluded.

In consequence, there is an increasing need for catalyst systems which can decrease the sulfur content of a hydrocarbon feedstock with a 95% boiling point of about 450°C or less to less than about 200 ppm, preferably less than

about 100 ppm, even more preferably less than about 50 ppm, calculated by weight as elemental sulfur on the total liquid product.

In the context of the present specification the term ultra-deep HDS means the reduction of the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm, preferably less than about 100 ppm, and even more preferably to a value of less than about 50 ppm, calculated by weight as elemental sulfur on the total liquid product, as determined in accordance with ASTM D-4294. The indications Group VIB and Group VIII correspond to the Periodic Table of Elements applied by Chemical Abstract Services (CAS system).

The problem associated with effecting this ultra-deep HDS is that the last sulfur compounds present in the feed are the hardest to remove.

Depending on their source, petroleum fractions can comprise various types of sulfur compounds. In hydrotreated middle distillate fractions, the major sulfur components are benzothiophenes and dibenzothiophenes. In straight-run materials significant quantities of other components are present, such as thiophenes, mercaptanes, sulfides, and disulfides. Of these, the sulfides and disulfides are the most reactive, followed by the thiophenes, benzothiophenes, and dibenzothiophenes. Within the group of dibenzothiophenes some components are more reactive than others. In consequence, in conventional hydrodesulfurisation (HDS), in which the sulfur level is reduced to a value of, say, about 0.3 wt.%, the sulfides and thiophenes are removed. In deep HDS, to a sulfur level of, say 200 to about 500 ppm, the benzothiophenes are removed. To effect ultra-deep HDS to a sulfur level of below about 200 ppm, the last compounds present, in particular a limited number of alkylated benzothiophenes, need to be removed in whole or in part, with the alkyldibenzothiophenes which have the alkyl on the 4- or 6- position being particularly difficult to remove.

It has been found that the reaction mechanisms by which these very refractive sulfur compounds are decomposed are different from those by which the less refractive compounds are decomposed. This is evidenced, e.g., by the fact that the catalysts which are known as particularly suitable for HDS appear to function less well in ultra-deep HDS. For example, conventionally, cobalt-molybdenum catalysts are more active in HDS than nickel-molybdenum catalysts. However, for ultra-deep HDS it has been found that nickel-molybdenum catalysts show better results than cobalt-molybdenum catalysts. Reference is made to the paper entitled "Ultra low sulfur diesel: Catalyst and Process options" presented at the 1999 NPRA meeting by T. Tippet et al.

The consequence of this difference in reaction mechanisms implies that the refiner who is faced with having to produce material with a lower sulfur content cannot just apply his usual hydrodesulfurisation catalyst under more stringent conditions. On the contrary, he will have to specifically select the hydrotreating catalyst that is most effective in effecting ultra-deep HDS. This is the more so since the reaction conditions necessary to effect ultra-deep HDS are rather severe in themselves, and the use of a dedicated catalyst makes it possible to select less severe reaction conditions, resulting in energy saving and a longer catalyst lifespan.

Catalysts which comprise a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive are known in themselves in the art.

For example, European patent application No. 0 300 629 and European patent application No. 0 357 295 describe hydrotreating catalysts comprising a support impregnated with at least one member of molybdenum, tungsten, and/or metals of Group VIII of the Periodic Table, and a mercapto-compound selected from mercaptocarboxylic acids, amino-substituted mercaptanes, di-

mercaptanes, and thioacids. The S-containing additive is incorporated into the catalyst composition to obviate the necessity of presulfiding, or to at least make the presulfiding less difficult.

European patent application No. 0 506 206 also describes a hydrotreating catalyst comprising an S-containing additive selected from the group of bi-mercaptanes, aminosubstituted mercaptanes, and thiocarboxylic acids. The S-containing catalyst is again intended to avoid the necessity of presulfiding. Some of the catalysts described in this reference are activated by a treatment with hydrogen at a temperature from room temperature up to 400°C, preferably 100-300°C.

Similar subject-matter is described in European patent application No. 0 338 788, and European patent application No. 0 289 211.

US 5,139,990 describes a hydrotreating catalyst comprising a carrier and hydrogenation metal components which is treated with an aqueous medium comprising a water-soluble or water-miscible S-containing organic additive, followed by drying the resulting catalyst and activating it with hydrogen at a temperature of 100-600°C.

US 4,636,487 describes a hydrotreating catalyst comprising a support and a hydroxymercaptide of one or more metals, which may be the reaction product of a mercaptoalcohol and one or more metal compounds. The catalyst may be activated with hydrogen at a temperature of 66-316°C.

European patent application No. 0 496 592 describes a hydrotreating catalyst comprising a carboxylic acid and an organic sulfur compound which may be a mercaptocarboxylic acid.

European patent application EP 1041133, describes effecting ultra-deep HDS with a catalyst comprising an O- or N-containing additive.

We have found that a catalyst which comprises a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive is particularly efficient in reducing the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm. In addition, this catalyst may make it possible to effect this ultra-deep HDS in combination with at least one of improved reduction of the amount of nitrogen, improved reduction of the total amount of aromatics present, and improved reduction of the amount of polynuclear aromatics. Preferably, the catalyst according to the invention shows ultra-deep HDS in combination with at least improved reduction of the amount of nitrogen, more preferably also in combination with improved reduction of the total amount of aromatics present, and improved reduction of the amount of polynuclear aromatics.

SUMMARY OF THE INVENTION

Accordingly, in one embodiment, the present invention is a process for reducing the sulfur content of a hydrocarbon feedstock having an initial boiling point of not less than about 100°C and a 95% boiling point of about 450°C or less and a sulfur content not greater than about 2 wt. % to a sulfur content of less than about 200 ppm. The invention comprises contacting the feedstock with a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive at a temperature from about 200 to about 450°C, a hydrogen partial pressure from about 5 to about 200 bar, a liquid hourly space velocity from about 0.1 to about 10 vol./vol.h and an H_2/oil ratio from about 50 to about 2000 Nl/l.

In a second embodiment, the present invention comprises the above first embodiment, except rath r than the feedstock being contacted with the catalyst comprising a Group VIB metal component, a Group VIII metal component, and

an S-containing organic additive, it is contacted with that catalyst after the catalyst is subjected to a sulfidation step and/or activation step.

In a third embodiment, the present invention comprises a two-step process for converting a starting feedstock having an initial boiling point of not less than about 100°C and a 95% boiling point of about 450°C or less and having a sulfur content of above about 0.1 wt.% and not greater than about 2 wt.% into a product having a sulfur content of about 200 ppm or less: The process comprises contacting the feedstock with a first catalyst followed by contact with a second catalyst, both catalysts comprising a Group VIB metal component and a Group VIII metal component, with at least the second catalyst additionally comprising an S-containing organic additive. The conditions for contact with both catalysts may be the same or different and comprise a temperature from about 200 to about 450°C, a hydrogen partial pressure from about 5 to about 200 bar, a liquid hourly space velocity from about 0.1 to about 10 vol./vol.h and an H_2/oil ratio from about 50 to about 2000 Nl/. The effluent from contact with the first catalyst has a sulfur content of less than about 0.1 wt.%, and the product after contact with the second catalyst has a sulfur content of less than about 200 ppm.

A fourth embodiment of the present invention comprises the above third embodiment, except rather than the feedstock being contacted with catalysts that comprise a Group VIB metal component and a Group VIII metal component, with at least the second catalyst additionally comprising an S-containing organic additive, the first catalyst and/or the second catalyst are subjected to a sulfidation step and/or activation step before contact, respectively, with the feedstock or contact with the effluent from contact with the first catalyst.

Other objectiv s and embodiments of the present invention encompass details about catalyst compositions, S-containing organic additive and sulfur

content of feedstock and product, all of which are hereinafter disclosed in the following discussion of each of the facets of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The additive-containing catalyst

In principle, the additive-containing catalyst can be any catalyst which comprises a Group VIB hydrogenation metal and/or a Group VIII hydrogenation metal, and an S-containing organic additive on a carrier. Catalysts comprising the combination of a Group VIB hydrogenation metal and a Group VIII hydrogenation metal are preferred.

As Group VIB metals suitable for use in the additive-containing catalyst for use in the process according to the invention may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. Catalysts comprising molybdenum as Group VIB metal component and nickel and/or cobalt as Group VIII metal component are preferred. For use in the process according to the invention catalysts comprising nickel may be preferred, especially when the feed comprises less than about 0.1 wt.% of sulfur. The catalyst usually has a metal content in the range of about 0.1 to about 50 wt.% calculated as oxides on the dry weight of the catalyst not containing the additive. The Group VIB metal will frequently be present in an amount of about 5 to about 40 wt.%, preferably about 15 to about 30 wt.%, calculated as trioxide. The Group VIII metal will frequently be present in an amount of about 1 to about 10 wt.%, preferably about 2 to about 7 wt.%, calculated as monoxide. The catalyst may also contain other components, such as phosphorus, halogens, and boron. Particularly, the presence of phosphorus in an amount of about 1 to about 10 wt.%, calculated as P_2O_5, may be preferred.

The catalyst carrier may comprise the conventional oxides, e.g., alumina, silica, silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and titania, as well as mixtures of these oxides. As a rule, preference is given to the carrier comprising alumina, silica-alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given to the carrier consisting essentially of alumina or alumina containing up to about 25 wt.% of other components, preferably silica. A carrier comprising a transition alumina, for example an eta, theta, or gamma alumina is preferred within this group, with a carrier comprising gamma-alumina being especially preferred. Additionally, although it is considered less preferred at present, the catalyst may contain 0 to about 60 wt.% of zeolite.

The catalyst's pore volume (measured via N2 adsorption) generally is in the range of about 0.25 to about 1 ml/g. The specific surface area will generally be in the range of about 50 to about 400 m^2/g (measured using the BET method). Generally, the catalyst will have a median pore diameter in the range of about 7 to about 20 nm, as determined by N2 adsorption. The figures for the pore size distribution and the surface area given above are determined after calcination of the catalyst at 500°C for one hour.

The catalyst is suitably in the form of spheres, pellets, beads, or extrudates. Examples of suitable types of extrudates have been disclosed in the literature (see, int. al., US 4,028,227). Highly suitable are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles (3 or 4 lobes).

The additive present in the catalyst may be any S-containing organic additive. In the context of the present specification the term organic additive refers to an additive comprising at least one carbon atom and at least one hydrogen atom.

Preferred compounds include the mercaptocarboxylic acids represented by the general formula HS-R1-COOR, wherein R1 stands for a divalent hydrocarbon group with 1 to about 10 carbon atoms and R stands for a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, or a linear or branched alkyl group having 1 to about 10 carbon atoms. Examples include mercaptoacetic acid (HS-CH2-COOH), beta-mercaptoproprionic acid (HS-CH2CH2-COOH), methylmercaptoacetate (HS-CH2-COOCH3), ethyl 2-mercaptoacetate (HS-CH2-COOC2H5), ethylhexyl mercaptoacetate (HS-CH2-COOC8H17), and methyl 3-mercaptoproprionate (HS-CH2CH2-COOCH3). Preferred compounds also include amino-substituted mercaptanes represented by the general formula H2N-R2-SH, wherein R2 stands for a divalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include 2-amino ethanethiol (H2N-CH2CH2-SH), and 4-amino thiophenol (H2N-C6H4-SH).

Preferred compounds also include di-mercaptanes represented by the general formula HS-R3-SH, wherein R3 stands for a divalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include ethanedithiol (HS-CH2CH2-SH) and 1,4-butanedithiol (HS-(CH2)4-SH). Preferred compounds also include thioacids of the formula R4-COSH, wherein R4 stands for a monovalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include thioacetic acid (CH3-COSH) and thiobenzoic acid (C6H5COSH). Dithioacids of the formula HSOC-R5-COSH wherein R5 is a divalent hydrocarbon group with 1 to about 15 carbon atoms may also be suitable. An example is dithioadipic acid (HSOC-C4H10-COSH). Preferred compounds also include mercaptoalcohols of the general formula R6S-R5-(OH)n, wherein R5 represents an alkyl group having from 1 to about 15 carbon atoms or a phenyl group, R6 represents a hydrogen atom or an alkyl group having 1 or about 2 carbon atoms, and n is 1 or about 2. Examples of these compounds include 2-mercaptoethanol, 2-(methylthio)ethanol, 2-

(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercaptophenol, 2-(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2,-propanediol, 3-methylthio-1,2, propanediol, and 3-ethylthio-1,2, propanediol. Other suitable compounds include sulfoxides of the formula R7-SO-R8, wherein R7 and R8 are hydrocarbon groups with 1 to about 5 carbon atoms. An example is dimethyl sulfoxide (CH3-SO-CH3).

Ammonium thiocyanate and thiourea may also be useful compounds, as may be the various dithiocarbamic acids and the salts thereof, such as ethylene bisdithiocarbamic acid and its salts, and dimethyl dithiocarbamic acid and its salts. Other suitable compounds include mercaptodiathiazoles and their salts, such as 2,5-dimercapto-1,3,4,-diathiazoles and its salts.

Other compounds which may be useful are (poly)sulfides of the formula R9-Sx-R10, wherein x is a value of 1 to about 15 and R9 and R10 are alkyl groups, preferably branched alkyl groups, with 1 to about 30 carbon atoms. Related compounds are those with the formula HO-R11-Sx-R12-OH, wherein x is a value of 1 to about 15 and R11 and R12 are alkyl groups with 1 to about 8 carbon atoms.

At this point in time the mercaptocarboxylic acids are considered preferred for reasons of activity. Other compounds, in particularly those that are soluble in or miscible with water, may be preferred for environmental reasons (less odour and/or no organic solvent necessary).

A single compound as well as a combination of compounds may be used as additive.

The amount of additive present in the additive-containing catalyst depends on the specific situation. It was found that the appropriate amount of additive gen rally lies in the range of about 0.01 to about 2.5 moles of additive per mole of hydrogenation metals present in the catalyst. If the amount of

additive added is too low, the advantageous effect associated with its presence will not be obtained. On the other hand, the presence of an exceptionally large amount of additive will not improve its effect. Generally, the aim is to select the amount of sulfur incorporated into the catalyst by way of the additive to correspond to about 5 to about 200%, preferably about 50 to about 200%, more preferably about 80 to about 150%, of the stoichiometric sulfur quantity necessary to convert the hydrogenation metals into Co_9S_8, MoS_2, WS_2, and Ni_3S_2, respectively.

The way in which the additive is incorporated into the catalyst composition is not critical to the process according to the invention. The additive may be incorporated into the catalyst composition prior to, subsequent to, or simultaneously with the incorporation of the hydrogenation metal components.

For example, the additive can be incorporated into the catalyst composition prior to the hydrogenation metal components by being added to the carrier before the hydrogenation metal components are. This can be done by mixing the additive with the carrier material before it is shaped, or by impregnating the shaped carrier material with the additive. This embodiment is not preferred at this point in time.

Alternatively, the additive can be incorporated into the catalyst composition simultaneously with the hydrogenation metal components. This can be done, e.g., by mixing the additive and the hydrogenation metal components with the carrier material before shaping or by impregnating the carrier with an impregnation solution comprising the hydrogenation metal components and the additive, followed by drying under such conditions that at least part of the additive is maintained in the catalyst.

It is also possible to incorporate the additive into the catalyst composition subsequent to the hydrogenation metal components. This can be done, e.g., by first incorporating the hydrogenation metal components into the catalyst composition, e.g., by mixing them with the carrier material or by impregnating the carrier with them, optionally followed by drying and/or calcining, and subsequently incorporating the additive, e.g., by impregnation.

Depending on the nature of the additive and the way in which it is incorporated into the catalyst composition, the additive may be used in the solid form, in the liquid form, or dissolved in a suitable solvent. It may be preferred for the additive to be incorporated into the catalyst dissolved in water.

The catalyst may be activated by contacting it with hydrogen at a temperature of about 100 to about 600°C as described in, e.g., EP 0 506 206, EP 0 338 788, EP 0 289 211, US 4,636,487, and US 5,139,990. Optionally, the catalyst may be contacted with an organic liquid either prior to or simultaneously with the contacting with hydrogen. Such a process is the subject of US patent application Serial No. 09/8296525, filed April 10, 2001, which is incorporated herein by reference.

If so desired, the catalyst may be subjected to a sulfiding step before its use in effecting ultra-deep HDS, said sulfiding step taking place *ex situ*, *in situ* or in a combination of *ex situ* and *in situ*. In the context of the present specification, the indication sulfiding step or sulfidation step is meant to include any process step in which a sulfur-containing compound is added to the catalyst composition and in which at least a portion of the hydrogenation metal components present in the catalyst is converted into the sulfidic form, either directly or after an activation treatment with hydrogen.

Suitable sulfidation processes are known in the art. *Ex situ* sulfidation processes take place outside the reactor in which the catalyst is to be used in

hydrotreating hydrocarbon feeds. In such a process the catalyst is contacted with a sulfur compound, e.g. a polysulfide or elemental sulfur, outside the reactor and, if necessary, dried. In a second step, the material is treated with hydrogen gas at elevated temperature in the reactor, optionally in the presence of a feed, to activate the catalyst, i.e. bring it into the sulfided state.

In situ sulfidation processes take place in the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. Here, the catalyst is contacted in the reactor at elevated temperature with a hydrogen gas stream mixed with a sulfiding agent, such as hydrogen sulfide or a compound, which under the prevailing conditions is decomposable into hydrogen sulfide. It is also possible to use a hydrogen gas stream combined with a hydrocarbon feed comprising a sulfur compound that under the prevailing conditions is decomposable into hydrogen sulfide. In the latter case it is possible to use a hydrocarbon feed comprising an added sulfiding agent (a so-called spiked feed), but it is also possible to use a sulfur-containing hydrocarbon feed without any added sulfiding agent, since the sulfur components present in the feed will be converted into hydrogen sulfide in the presence of the catalyst. The hydrocarbon feed may be the feed to be subjected to ultra-deep HDS in the process according to the invention, but it may also be a different feed, later to be replaced with the feed to be subjected to ultra-deep HDS. Combinations of the various sulfiding techniques may also be applied. In the context of the present invention it may be preferred to sulfide the catalyst by contacting it with an, optionally spiked, hydrocarbon feed.

A further process for presulfiding catalysts comprising an organic S-containing catalyst is the subject of US patent application No. 09/829,626, filed April 10, 2001, which is incorporated herein by reference. This patent application is directed to a presulfiding process in which a catalyst comprising a sulfur-containing additive is presulfided in two steps, the first step being carried out at a lower temperature than the second step. US patent application Serial

No. 09/829640, filed April 10, 2001, which is incorporated herein by reference, also describes a suitable presulfiding procedure for catalysts containing an S-containing additive. In the process described in this reference the presulfiding is carried out ex-situ.

Another process, which may be preferred over those of the two above-mentioned references is described in US patent application Serial No. 09/829624, filed April 10, 2001, which is also incorporated herein by reference. This patent application is directed to a presulfiding process in which a catalyst comprising a sulfur-containing additive is first contacted with an organic liquid followed by being contacted with hydrogen and a sulfur-containing compound in the gaseous phase.

The feed

The feedstock suitable for use in the process according to the invention has a 95% boiling point, as determined in accordance with ASTM D-2887, of about 450°C or less, preferably about 420°C or less, more preferably about 400°C or less. That is, 95 vol.% of the feedstock boils at a temperature of about 450°C or less, preferably about 420°C or less, more preferably about 400°C or less. Generally, the initial boiling point of the feedstock is not less than about 100°C, preferably not less than about 180°C.

The feedstock to be used in the process according to the invention may or may not have been subjected to a previous hydrodesulfurisation step, depending on the envisaged process conditions.

If the reaction conditions can be selected suitable for more severe hydrotreating, the catalyst used in the process of the invention is sufficiently active to be able to convert fractions with a sulfur content of, e.g., about 0.1 wt.% ppm to about 2 wt.%, preferably 1 to about 2 wt.%, into product with a

sulfur content less than about 200 ppm, preferably less than about 100 ppm, more preferably, less than about 50 ppm. Such feedstocks generally contain about 20 to about 1200 ppm nitrogen, preferably about 30 to about 800 ppm, more preferably about 70 to about 600 ppm. The metal content of such feedstocks preferably is less than about 5 ppm, more preferably less than about 1 ppm (Ni+V). Examples of suitable feedstocks of this type are feedstocks comprising one or more of straight run gas oil, light catalytically cracked gas oil, and light thermally cracked gas oil, and (mild) hydrocracked oils.

On the other hand, the invention is also suitable for the ultra-deep hydrodesulfurisation of hydrocarbon feeds of the above description which had already been subjected to a hydrotreating operation, and which have sulfur contents of generally less than about 0.1 wt.%, more specifically about 150 to about 500 ppm. [Obviously, applying the process according to the invention to feeds with a sulfur content less than about 200 ppm will only be useful if a sulfur content below that value is desired, e.g., less than about 100 ppm, or less than about 50 ppm.]

If it is desired to subject the above-mentioned starting hydrocarbon feedstock to a first hydrotreating (hydrodesulfurisation) step to reduce its sulfur content to a value less than about 0.1 wt.%, this can be carried out in various ways. One can, e.g., use a conventional hydrodesulfurisation catalysts comprising a Group VIB metal component, a Group VIII metal component, and, optionally, phosphorus on a carrier comprising alumina. Suitable hydrodesulfurisation catalysts are commercially available, and include for example KF 756 and KF 901 of Akzo Nobel. It is also possible to effect such first hydrodesulfurisation step by means of a two-step process, such as those described in EP 0 464 931, EP-A 0 523 679 or EP 870 807. If so desired, one may also use an additive-based catalyst to effect such first hydrodesulfurisation step.

The present invention also pertains to a two-step process for converting a starting feedstock having a sulfur content of above about 0.1 wt.% into a product having a sulfur content of less than about 200 ppm, wherein the process comprises optionally sulfiding and/or activating a first and a second catalyst comprising a Group VIB metal component and a Group VIII metal component, with at least the second catalyst additionally comprising an S-containing organic additive, contacting a feedstock with a 95% boiling point of about 450°C or less and a sulfur content of about 0.1 wt.% or more with the first catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 0.1 wt.%, preferably less than about 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, with the second catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm, preferably less than about 100 ppm, more preferably less than about 50 ppm.

It is considered preferred at this point in time for the first catalyst to comprise molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, with the second catalyst comprising molybdenum as Group VIB metal component and nickel as Group VIII metal component. The two-step process can be carried out in one or two reactors, as may be desired. If both catalysts contain an organic additive, the two catalysts may be the same or different.

<u>The process conditions</u>

The process according to the invention is carried out at elevated temperature and pressure. The temperature generally is about 200 to about 450°C, preferably about 280 to about 430°C. The reactor inlet hydrogen partial pressure generally is about 5 to about 200 bar, preferably about 10 to about

100 bar, more preferably about 15 to about 60 bar. The liquid hourly space velocity preferably is between about 0.1 and about 10 vol./vol.h, more preferably between about 0.5 and about 4 vol./vol.h. The H_2/oil ratio generally is in the range of about 50 to about 2000 Nl/l, preferably in the range of about 80 to about 1000 Nl/l. For the two-step process described above, the reaction conditions for both steps may be selected independently from each other, taking the above-mentioned general and preferred ranges into account.

The process conditions are selected in such a way that the sulfur content of the total liquid effluent is less than about 200 ppm, preferably less than about 100 ppm, more preferably less than about 50 ppm. The exact process conditions will depend, int. al., on the nature of the feedstock, the desired degree of hydrodesulfurisation, and the nature of the catalyst. In general, a higher temperature, a higher hydrogen partial pressure, and a lower space velocity will decrease the sulfur content of the final product. The selection of the appropriate process conditions to obtain the desired sulfur content in the product is well within the scope of the person skilled in the art of hydroprocessing.

Example 1

Preparation of additive-containing catalyst

Extrudates of a gamma-alumina carrier were impregnated to pore volume saturation with an impregnation solution comprising a molybdenum compound, a nickel compound, and phosphoric acid, after which the impregnated carrier was dried at a temperature of 140°C for a period of 16 hours. The dried extrudates were impregnated with a solution of thioglycolic acid (TGA), and dried. The final catalyst contained 20 wt.% of molybdenum, calculated as trioxide, 5 wt.% of nickel, calculated as oxide, and 7 wt.% of phosphorus, calculated as P_2O_5. All weight percentages are calculated on the

dry catalyst base, not including the additive. The molar ratio between TGA and the total of Ni and Mo is 0.4.

The catalyst according to the invention was tested in an upflow tubular reactor side by side with commercial catalyst KF 756 of Akzo Nobel. Each reactor tube contained 75 ml of catalyst homogeneously intermixed with 70 ml of carborundum particles. The catalysts were sulfided using the feed specified below in which dimethyl disulfide had been dissolved to a total S content of 2.5 wt.%.

The feed applied was a Kuwait petroleum gas oil feedstock with the following properties.

Nitrogen (ASTM D-4629) (ppmwt)	86
Sulfur (ASTM D-4294) (ppmwt)	1.2 wt.%
Density 15°C (g/ml)	0.84
Dist. (°C)	ASTM D-86
IBP	184
5 vol.%	219
10 vol.%	231
30 vol.%	265
50 vol.%	287
70 vol.%	310
90 vol.%	345
95 vol.%	360
FBP	373

The catalysts were tested under the two test conditions given below.

	Condition 1	Condition 2
pressure (bar)	40	20
Temperature (°C)	330	340
LHSV (h-1)	2	1.5
H_2/oil ratio (Nl/l)	300	300

The products from the different runs were analysed. The results thereof are given below.

Condition 1

	Catalyst according to the invention	Comparative catalyst
product S (ppm)	21	279
product N (ppm)	0.9	14

Condition 2

	Catalyst according to the invention	Comparative catalyst
product S (ppm)	51	132
product N (ppm)	5	35

This example shows that the catalyst according to the invention which contains an S-containing additive gives a much lower S and N level in the final product than the comparative commercial catalyst.